

10.0

Best Available Copy



מדינת ישראל
STATE OF ISRAEL

Ministry of Justice
Patent Office

PCT/IL 03 / 00 058
Rec'd CT/PTO 22 JUL 2004
10/502267

REC'D 03 MAR 2003	
WIPO	PCT

משרד המשפטים
לשכת הפטנטים

This is to certify that
annexed hereto is a true
copy of the documents as
originally deposited with
the patent application
of which particulars are
specified on the first page
of the annex.

זאת לתעודה כי
רצופים בזה העתקים
נכונים של המסמכים
שהופקדו לכתחילה
עם הבקשה לפטנט
לפי הפרטים הרשומים
בעמוד הראשון של
הנספח.



PRIORITY DOCUMENT
SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH
RULE 17.1(a) OR (b)

This 13-02-2003 היום

המנהל הכללי
לפטנטים

רשם הפטנטים

Commissioner of Patents

נתאשר
Certified

PG/1105/00058

לשימוש הלישכה
For Office Use

חוק הפטנטים, תשכ"ז-1967
Patent Law, 5727 - 1967
בקשה לפטנט
Application for Patent

מספר: Number	147945
תאריך: Date	31-01-2002
הוקדם/נדחה Ante/Post-Dated	

אני, (שם המבקש, מענו ולגבי גוף מאוגד - מקום התאגדות)

I, (Name and address of applicant, and in case of body corporate-place of incorporation)

Inventors: הממציאים:
1. זילברמן יוסי
Joseph ZILBERMAN
2. כנפי דורית
Dorit CANFI
3. דוד יפה
David IOFFE
4. גרגורי טיטלמן
Gregory TITELMAN
5. שמואל ברון
Samuel BRON
6. אולגה ויינברג
Olga WEINBERG

BROMINE COMPOUNDS LTD תרכובות ברום בע"מ
MAKLEFF HOUSE. בית מקלף
P.O. Box 180 ת.ד. 180
Beer-Sheva באר-שבע

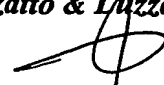
בעל ההמצאה מכח THE LAW הדין
an invention the title of which is Owner, by virtue of

חומרים חדשים עמידים נגד אש

(בעברית)
(Hebrew)
(באנגלית)
(English)

NEW FIRE RETARDANTS

המבקש בואת כי ינתן לי עליה פטנט hereby apply for a patent to be granted to me in respect thereof.

*בקשת חלוקה - Application of Division		*בקשת פטנט מוסף - Application for Patent Addition		*דרישה דין קדימה Priority Claim	
מבקשת פטנט from Application		לבקשה/לפטנט to Patent/Apl.		מספר/סימן Number/Mark	תאריך Date
מס' _____ dated _____		מס' _____ dated _____			
*יפוי כח: כללי / מיוחד - רצוף בזה / עוד יוגש P.O.A.: general / individual - attached / to be filed later הוגש בענין 79359 filed in case					
המען למסירת מסמכים בישראל Address for Service in Israel לוצאטור את לוצאטור ת.ד. 5352 מספרנו: 14128/02 באר שבע 84152					
חתימת המבקש Signature of Applicant				היום 29 בחודש ינואר שנה 2002 of the year of This	
Luzzatto & Luzzatto By:  Attorneys for Applicant				לשימוש הלישכה	

טופס זה כשהוא מוטבע בחותם לישיבת הפטנטים ומושלם במספר ובתאריך ההגשה, הינו אישור להגשת הבקשה שפרסיה ושומים לעיל.

Ref:14128/02

חומרים חדשים עמידים נגד אש

NEW FIRE RETARDANTS

NEW FIRE RETARDANTS

Field of the Invention

The present invention provides novel pentabromobenzyl alkyl ethers serving as highly effective flame retardants in polymers. The invention further provides a fire retarded polymer composition comprising said pentabromobenzyl alkyl ethers. The terms fire retardants and flame retardants are used herein synonymously.

Background of the Invention

Compounds containing a pentabromobenzyl moiety are known to be flame retardants. Pentabromobenzyl acrylate (EP 481126), pentabromobenzyl terephthalate (DE 33 20 333), and pentabromobenzyl tetrabromophthalate (EP 47866) are reported to be used in flame retardant polymer compositions. All the above mentioned compounds are esters of carboxylic acids. It is generally known that the ester group is rather unstable to hydrolysis, especially in the presence of acids and bases. This hydrolytic decomposition of esters precludes their use in a great number of applications.

While it is generally recognized that compositions containing bromine improve the flame retardancy of polymers, many bromine-containing compounds are unsatisfactory due to their instability. Such compounds are known to undergo dehydrobromination when incorporated in polymers.

Therefore there is a demand for fire retardants retaining their stability against hydrolysis, especially in the presence of acids and bases. In addition, there is a demand for bromine-containing fire retardants having stability against dehydrobromination when incorporated in polymers.

It is an object of present invention to provide a bromine-containing fire retardant, which has excellent fire-retardancy properties.

It is another object of present invention to provide such fire retardant retaining its stability against hydrolysis and/or decomposition in the presence of an acid or a base.

It is yet a further object of present invention to provide such fire retardant eliminating the undesired dehydrobromination process when incorporated in polymers.

It is yet a further object of present invention to provide fire retarded polymeric and polymer-containing compositions comprising such bromine-containing fire retardant.

The present invention provides novel pentabromobenzyl alkyl ethers possessing highly satisfactory flame retarding characteristics (properties) while retaining their stability against undesired processes, such as dehydrobromination and hydrolysis. The invention further provides

polymeric and polymer-containing compositions containing the said novel pentabromobenzyl alkyl ether,s that exhibit excellent fire retardancy.

Other objects and advantages of the invention will become apparent as the description proceeds.

Summary of the Invention

The present invention provides novel pentabromobenzyl alkyl ethers. It further provides a process for the preparation of said novel compounds by the reaction of aliphatic mono- or di-alcohols or the corresponding metal alcoholates with pentabromobenzyl halide, preferably bromide. The pentabromobenzyl alkyl ethers of this invention possess good hydrolytic and thermal stability and are useful as flame retardants in thermoplastic and thermosetting resins. The present invention further provides a fire retarded polymeric and polymer-containing compositions comprising said novel pentabromobenzyl alkyl ethers.

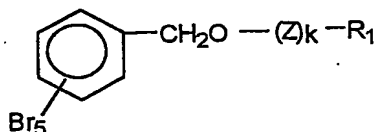
All the above and other characteristics and advantages of the invention will be better understood through the following illustrative and non-limitative detailed description of the preferred embodiments thereof.

Detailed Description of Preferred Embodiments

The pentabromobenzyl alkyl ethers of the present invention are prepared by the reaction of pentabromobenzyl halide, preferably bromide (PBBBr) with

an aliphatic mono- or di-alcohol (or the corresponding metal alcoholate), in the presence or absence of a base.

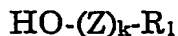
The novel pentabromobenzyl alkyl ethers of the present invention have the following formula:



wherein:

- Z represents the group $-(Y-O)_n-$, wherein Y is a linear or branched $-(C_2-C_8)$ alkylene-, preferably $-CH_2CH_2-$ and $-CH_2CH(CH_3)-$;
 - n represents an integer from 2 to 4;
 - k may be 0 or 1;
 - R_1 represents hydrogen, a linear or branched $-(C_1-C_{10})$ alkyl, a linear or branched $-(C_2-C_{10})$ alkylene-OH, allyl, or 1,2-dibromopropyl;
- provided that when k is zero R_1 represents a linear or branched $-(C_4-C_{10})$ alkyl or a linear or branched $-(C_2-C_{10})$ alkylene-OH and when k is 1, R_1 represents hydrogen, a linear or branched $-(C_1-C_4)$ alkyl, allyl or 1,2-dibromopropyl.

Aliphatic alcohols (or the corresponding metal alcoholates) which are reacted with pentabromobenzyl halide, preferably PBBBr, to obtain the pentabromobenzyl alkyl ethers of present invention may be represented by the formula:



wherein Z, R₁ and k are as defined above.

Aliphatic alcohols of the above formula used in the process for preparing the compounds of present invention include, *inter alia*, glycols such as ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, tetrapropylene glycol, and monoethers of these glycols such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl and allyl ether. Other aliphatic alcohols used in said process may be straight chained and branched alcohols such as butanols, pentanols, hexanols, octanols, nonanols, decanols.

Aliphatic di-alcohols also applicable, for example 1,3-propane diol, 1,4-butane diol, 1,5-pentane diol, 1,6-hexane diol, 1,7-heptane diol, 1,8-octane diol, 1,9-nonane diol, 1,10-decane diol.

In a preferred embodiment the reaction of PBBBr and the aliphatic alcohol is carried out in the presence of a strong base such as sodium hydroxide or potassium hydroxide, in a medium of either an organic solvent or an excess aliphatic alcohol. The organic solvent is selected from aromatic compounds. Especially suitable aromatic solvents are chlorobenzene, ortho-dichlorobenzene, bromobenzene, mesitylene, and in particular, toluene and xylene.

An effective amount of the base employed in the process is in a range of 1-1.5 mol per 1 mol PBBBr, and preferably 1-1.2 mol.

When an aromatic solvent is used, the amount of a glycol monoether of the formula $\text{HO}-(\text{Z})_k\text{-R}_1$

wherein Z represents $-(\text{Y-O})_n-$, or of an alcohol in which k is zero may be in the range of 1-4 mol alcohol, and preferably between 1.5-3 mol, per 1 mol PBBBr.

When the reaction is carried out in an excess of reacting alcohol of the formula $\text{HO}-(\text{Z})_k\text{-R}_1$ also used as a solvent, the amount of alcohol is preferably expressed in weight percent in relation to the amount of PBBBr. Thus, the excess of alcohol in such cases is from 200 up to 1000% by weight, and preferably 400-700% by weight, over the amount of PBBBr used. An excess of alcohol below 200% by weight makes carrying out the reaction rather cumbersome and problematic due to the difficulty of stirring the highly concentrated suspension of PBBBr in the alcohol. Using an excess of alcohol greater than 1000% by weight over the amount of PBBBr is inexpedient due to the need of recycling a large quantity of alcohol.

Regardless of the presence or absence of the aromatic organic solvent the amount of glycol of the formula $\text{HO}-(\text{Z})_k\text{-R}_1$, wherein Z represents $-(\text{Y-O})_n-$, (R_1 is H and Y and n are as defined above) or dialcohols of the formula $\text{HO}-(\text{Z})_k\text{-R}_1$, wherein k is zero and R_1 represents a linear or

branched $-(C_2-C_{10})$ alkylene-OH, comprises between 5-18 mol, and preferably between 10-15 mol per 1 mol PBBBr. The relatively large excessive amounts of these alcohols are required for minimizing the formation of undesirable di-ethers, namely di-pentabromobenzyl ethers of glycols and diols. Using a molar ratio greater than 18 mol alcohol per 1 mol PBBBr is inexpedient due to the need to recycle a larger quantity of alcohol.

Said reactions are carried out at a temperature of between 40 and 150°C, and preferably between 50 and 110°C. Applying a temperature lower than 40°C resulted in a low yield. On the other hand, applying a temperature higher than 150°C is not advisable since at such temperatures undesirable decomposition products are formed in the presence of a strong base.

Sodium or potassium hydroxide is employed in a solid form. Water should be eliminated from the reaction mixture as much as possible. When aqueous solutions of hydroxides are used the main reaction products are pentabromobenzyl alcohol and di-pentabromobenzyl ether.

The reaction may also be conducted without a base. However, due to the fact that PBBBr is considerably less reactive towards alcohols in the absence of a strong base, the reaction must be carried out at a temperature of between 170 and 220°C. Applying such high temperatures favors the formation of undesired decomposition products.

The following examples illustrate specific embodiments of both the preparation of certain compounds of the invention and the utility of these compounds as flame retardants in various polymer resins. The following examples should not be construed as limiting the scope thereof.

Example 1

A 2 liter reactor, equipped with a mechanical stirrer, a thermometer and a reflux condenser, is charged with PBBBr (212 g, 0.37 mol) and 2-methoxyethanol (700 g, 10 mol). The slurry formed is heated to 105°C, followed by addition of potassium hydroxide powder (25.7 g, 0.39 mol). The resulting mixture is heated for 3 hours at 105°C, with vigorous stirring until the PBBBr conversion is complete (confirmed by HPLC analysis). The solids are filtered at room temperature and washed with water (300 g) to remove potassium bromide. After vacuum drying of the remaining solid, there are obtained 182 g (83% of theoretical) of 1-methoxy-2-pentabromobenzyloxyethane [pentabromobenzyl-O-CH₂-CH₂OCH₃] in the form of a white solid powder, melting point 145-146°C. HPLC analysis shows the purity to be 100% (area %). The unreacted 2-methoxyethanol is recovered by stripping off the ethanol and can be used repeatedly.

Example 2

A 2 liter reactor, equipped with a mechanical stirrer, a thermometer, and a reflux condenser, is charged with PBBBr (500 g, 0.88 mol), 2-butoxyethanol (212 g, 1.8 mol) and toluene (800 ml). The slurry formed is heated to 55°C,

followed by addition of sodium hydroxide powder (38 g, 0.9 mol). The resulting mixture is heated for 3 hours at 55°C, with vigorous stirring until the PBBBr conversion is complete (confirmed by HPLC analysis). The final reaction mixture is cooled to room temperature, sodium bromide formed is filtered off and the toluene is fully stripped off. The remaining viscous liquid is mixed with ethanol (1 l) at 75°C and a by-product constitutes bis-(pentabromobenzyl) ether which does not dissolve in ethanol, is removed by hot filtration. After crystallization, filtration and vacuum drying, there is obtained 426 g (80% of theoretical) of 1-butoxy-2-pentabromobenzyloxyethane [pentabromobenzyl-O-CH₂CH₂O(CH₂)₃CH₃] in the form of a white solid powder, melting point 67°C. The HPLC analysis shows the purity to be 100% (area %). The unreacted 2-butoxyethanol is recovered by stripping off the ethanol and can be used repeatedly.

Example 3

A 0.25 liter reactor, equipped with a mechanical stirrer, a thermometer, and a reflux condenser, is charged with the monomethyl ether of diethylene glycol (12 g, 0.1 mol), NaOH (1.6 g, 0.038 mol) and ortho-xylene (80 ml). The reactor contents are heated to 70°C, followed by addition of PBBBr (20 g, 0.035 mol). The resulting mixture is heated for 2 hours at 70°C with vigorous stirring until the PBBBr conversion is complete (HPLC analysis). The treatment of the final reaction mixture is carried out as described in Example 1. There is obtained 15.9 g (75% of theoretical) of 1-(pentabromophenyl)-2,5,8-trioxanonane [pentabromobenzyl-O-(CH₂CH₂O)₂CH₃] in

the form of a white solid powder, melting point 83°C. HPLC analysis shows the purity to be 99.5% (area %).

Example 4

A 2 liter reactor, equipped with a mechanical stirrer, a thermometer, and a reflux condenser, is charged with diethylene glycol (637 g, 6 mol) and solid sodium hydroxide (16.8 g, 0.42 mol). The mixture is heated to 80°C, followed by portion-wise addition of PBBBr (226.2 g, 0.4 mol) over a period of 1.5 h. The reaction slurry is heated for one more hour with vigorous stirring until the PBBBr conversion is complete (confirmed by HPLC analysis). Ethanol (0.75 l) is added and the precipitated solid is washed thoroughly with 1 l of 50% aq. ethanol. After vacuum drying there is obtained 217 g (92% of theoretical) of 3,6-dioxa-7-(pentabromophenyl)-heptanol-1 [pentabromobenzyl-O-(CH₂CH₂O)₂H] in the form of a white solid, melting point 117-120°C. HPLC analysis shows the purity to be 98% (area %). The product contains 2% diethylene glycol dipentabromobenzyl ether.

Example 5

A 2 liter reactor, equipped with a mechanical stirrer, a thermometer and a reflux condenser, is charged with PBBBr (453 g, 0.8 mol) and 1,6-hexane diol (1134 g, 9.6 mol). The slurry formed is heated to 85°C, followed by addition of sodium hydroxide powder (36 g, 0.88 mol). The resulting mixture is heated at 85°C for 4 hours with vigorous stirring until the PBBBr conversion is complete (confirmed by HPLC analysis). The excess diol is

distilled off under vacuum (1 mm Hg, 100-105°C) and can be used repeatedly. The residue is treated with refluxing acetonitrile (1 l) followed by hot filtration to remove sodium bromide and bis(pentabromobenzyl) ether. After crystallization, filtration and vacuum drying there is obtained 337 g (70% of theoretical) of 6-(pentabromobenzyloxy)-hexanol-1 [pentabromobenzyl-O-(CH₂)₆OH] in the form of a white solid powder, melting point 81-83°C. HPLC analysis shows the purity to be 98% (area %).

Example 6

A 1 liter reactor, equipped with a mechanical stirrer, a thermometer and a reflux condenser, is charged with 2-ethylhexanol-1 (68.3 g, 0.525 mol), toluene (400 ml) and potassium hydroxide (17.3 g, 0.26 mol). The reactor contents are heated to 90°C, followed by addition of PBBBr (102 g, 0.18 mol). The reaction mixture is heated for 5 hours at 90°C with vigorous stirring until the PBBBr conversion is complete (confirmed by HPLC analysis). The final reaction mixture is cooled to room temperature, sodium bromide is filtered off and the toluene is fully stripped. The remaining viscous liquid is mixed with 0.15 l ethanol-water (80:20) at 75°C and bis(pentabromobenzyl) ether is removed by hot filtration. After crystallization in an ice bath, filtration and vacuum drying there is obtained 88.7 g (80% of theoretical) of pentabromobenzyl 2-ethylhexyl ether [pentabromobenzyl-O-CH₂CH(C₂H₅)-(CH₂)₃CH₃]. The final product is in the form of a white wax at room temperature. HPLC analysis shows the purity to be 99 % (area %).

Example 7

A 0.25 liter reactor, equipped with a mechanical stirrer, a thermometer, a reflux condenser and a Dean-Stark trap, is charged with 2-allyloxyethanol (7.2 g, 0.07 mol), toluene (100 ml) and sodium hydroxide (1.5 g, 0.037 mol). The reactor contents are heated to reflux and the water formed is removed as an azeotrope with toluene. After cooling down of the reactor contents to 90°C PBBBr (20 g, 0.035 mol) is added and after heating at 90°C for 1 hour the PBBBr conversion is complete (confirmed by HPLC analysis). The final reaction mixture is cooled to room temperature, sodium bromide is filtered off and the toluene is fully stripped. The crystallization of the residue from ethanol-dichloroethane (3:1) affords 16.8 g (81% of theoretical) of 1-allyloxy-2-pentabromobenzyloxyethane [pentabromobenzyl-O-CH₂CH₂OCH₂CH=CH₂] in the form of a beige solid powder, melting point 87-88°C. HPLC analysis shows the purity to be 99.6% (area %).

The novel compounds of the present invention are highly efficient flame retardants when incorporated into various polymers or polymer-containing compositions. In general, the novel compounds of present invention are useful as flame retardants in a wide variety of polymeric compositions such as, for example, chlorinated polyethylene, polyethylene, polypropylene, styrene resins, high-impact polystyrene, polyvinyl chloride, acrylonitrile-butadiene-styrene copolymer, flexible and rigid polyurethanes, epoxy resins, unsaturated polyester resins and the like. In particular, the compounds of present invention are highly effective flame retardants in polyurethanes.

The novel compounds of the invention are also useful as fire retardants when incorporated into polymer-containing compositions. Such compositions as used herein are polymeric compositions that also comprise other constituents (other than the fire retardants of the invention). Such constituents may be, but are not limited to, catalysts, antioxidants, anti-dripping agents and the like. In the polymer-containing compositions the polymeric constituent may be any one of the above-mentioned polymers.

The amount of novel compound of present invention which is necessary for conferring commercially satisfactory flame retardancy to a particular polymer or polymer-containing composition may vary over a wide range. Usually, the flame retardant material of present invention is employed in an amount of between about 1 to 50% by weight of the polymer. Preferably, between about 3 to about 30% is used. In general, any suitable known method of incorporating flame retardants to polymer materials may be employed.

The following examples demonstrate the utility of the pentabromobenzyl alkyl ether of the present invention as a flame retardant in various polymers.

Example 8

In this example polypropylene (block copolymer of polypropylene with propylene-ethylene rubber, Capilene SG-50, a trade mark of Carmel Olefins)

in a granulated form was used as the polymer resin. Different pentabromobenzyl alkyl ethers, each in amount corresponding to 22 wt% of bromine and 11 wt% of antimony oxide as a synergist, were admixed with the polypropylene. Regular amounts of antioxidants and anti-dripping agents, when applied, were added to the mixture at the expense of the polymer. Mixing was done in a Brabender internal mixer of 55 cm³ volume capacity at 50 rotations per minute and 190°C for various periods. Specimens of 3.2 mm thickness were prepared by compression molding in a hot press at 200°C, cooling to room temperature and cutting into standard test pieces.

The flammability was tested by the limiting oxygen index method (hereinafter referred to as "LOI") in accordance with ASTM D-2863-99. LOI is defined as the minimum concentration of oxygen (%vol) in a mixture of oxygen and nitrogen that will just support combustion of the fire retarded polymer under the conditions of the test procedure. The utility of pentabromobenzyl alkyl ethers as flame retardants is shown in Table 1: all formulations containing pentabromobenzyl alkyl ethers have a significantly larger LOI than the neat polymer.

Table 1

Flame retardant*	Wt. %	LOI, O ₂ %
None	0.0	16.7
Ether of Example 1	30.8	23.5
Ether of Example 2	33.7	23.0
Ether of Example 5	34.4	22.8
Ether of example 6	33.7	22.0

* Each formulation contains 22% wt bromine

Example 9

In this example, polystyrene (either a High Impact Polystyrene (HIPS) - Styron 472, a trade mark of Dow, or a Acryl-Butadiene-Styrene terpolymer (ABS) - Magnum 3404, a trade mark of General Electric) was used as the polymer resin. Different pentabromobenzyl alkyl ethers in various amounts corresponding to a bromine content of 6%, 11% or 12%, and antimony oxide as a synergist, as shown in Table 2, were admixed with the polymer in a granulated form. Regular amounts of antioxidants and anti-dripping agents, when applied, were added to the mixture at the expense of the polymer. Mixing was done in a Brabender internal mixer of 55 cm³ volume capacity at 50 rotations per minute and 200°C for the desired time. Specimens of 3.2 mm or 1.6 mm thickness were prepared by compression molding in a hot press at 200°C, cooling to room temperature and cutting into standard test pieces. The flammability was tested by the limiting oxygen index method (as

described above) in accordance with ASTM D-2863, and by the UL-94 test (Underwriters Laboratories) with bottom ignition for two successive 10-second intervals by a standard burner flame. Five test-pieces of each composition were tested under the conditions of the UL-94 procedure. A wide range of flame retardancy of styrene polymers can be achieved (UL-94 rating V-2 or V-0) at 1.6 and 3.2 mm thickness, indicating that the novel pentabromobenzyl alkyl ethers of present invention provides a high level of fire retardancy efficiency.

Table 2

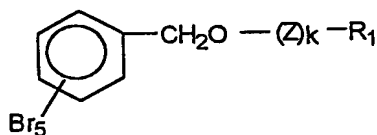
Flame retardant	Polymer type	Ether Wt%	Bromin Wt%	Sb ₂ O ₃ Wt%	LOI O ₂ %	UL-94 3.2 mm	UL-94 1.6 mm
None	ABS	0	0	0	18.0	NR	NR
None	HIPS	0	0	0	17.8	NR	NR
Ether of Example 1	HIPS	15.4	11.0	6.0	24.4	V-0	
	ABS	15.4	11.0	6.0	24.8	V-0	
	HIPS	16.8	12.0	6.0	25.1		V-0
Ether of Example 2	HIPS	16.9	11.0	6.0	23.8	V-0	
	HIPS	9.2	6.0	3.0	21.8		V-2
Ether of Example 6	HIPS	16.9	11.0	6.0	23.2	V-0	
	HIPS	9.2	6.0	3.0	21.4		V-2
Ether of Example 5	HIPS	17.2	11.0	6.0	24.0	V-0	
	ABS	17.2	11.0	6.0	24.8	V-0	
	HIPS	18.2	12.0	6.0	24.7		V-0
Ether of Example 4	ABS	17.9	12.0	6.0	-		V-0
	HIPS	17.9	12.0	6.0	-		V-0

While the invention has been described herein above with regard to certain illustrative, specific embodiments, it should be pointed out that many modifications and variations are possible in the light of the above teaching. It is understood therefore, that the invention may be practiced otherwise

than as specifically described without departing from the spirit and scope of the invention.

CLAIMS

1. A pentabromobenzyl alkyl ether of the formula:



wherein:

- Z represents the group $\text{---(Y---O)}_n\text{---}$, wherein Y is a linear or branched $\text{---(C}_2\text{---C}_8\text{)alkylene---}$, preferably $\text{---CH}_2\text{CH}_2\text{---}$ and $\text{---CH}_2\text{CH(CH}_3\text{)---}$;
 - n represents an integer from 2 to 4;
 - k may be 0 or 1;
 - R₁ represents hydrogen, a linear or branched $\text{---(C}_1\text{---C}_{10}\text{)alkyl}$, a linear or branched $\text{---(C}_2\text{---C}_{10}\text{)alkylene---OH}$, allyl, or 1,2-dibromopropyl;
- provided that when k is zero R₁ represents a linear or branched $\text{---(C}_4\text{---C}_{10}\text{)alkyl}$ or a linear or branched $\text{---(C}_2\text{---C}_{10}\text{)alkylene---OH}$ and when k is 1, R₁ represents hydrogen, a linear or branched $\text{---(C}_1\text{---C}_4\text{)alkyl}$, allyl or 1,2-dibromopropyl.

2. A pentabromobenzyl alkyl ether according to claim 1, wherein Z represents the group $\text{---CH}_2\text{CH}_2\text{O---}$.

3. A pentabromobenzyl alkyl ether according to claim 1, wherein $k=1$ and R₁ represents H, methyl or butyl.

4. A pentabromobenzyl alkyl ether according to claim 1, wherein $k=0$ and R_1 represents branched (C_8) alkyl or linear (C_6) alkylene-OH.

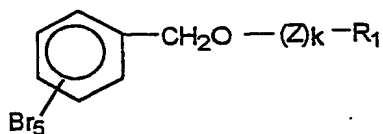
5. A pentabromobenzyl alkyl ether according to claim 1, selected from the group consisting of:

- (i) pentabromobenzyl-O-CH₂-CH₂OCH₃;
- (ii) pentabromobenzyl-O-CH₂CH₂O(CH₂)₃CH₃;
- (iii) pentabromobenzyl-O-(CH₂CH₂O)₂CH₃;
- (iv) pentabromobenzyl-O-(CH₂CH₂O)₂H;
- (v) pentabromobenzyl-O-(CH₂)₆OH;
- (vi) pentabromobenzyl-O-CH₂CH(C₂H₅)(CH₂)₃CH₃; and
- (vii) pentabromobenzyl-O-CH₂CH₂OCH₂CH=CH₂.

6. A compound according to any one of claims 1 to 5, for use as a fire retardant.

7. A compound according to any one of claims 1 to 5, for use as a fire retardant in a polymeric composition or in polymer-containing composition.

8. A fire retarded polymeric or polymer-containing composition comprising a pentabromobenzyl alkyl ether of the formula:



wherein Z, R₁ and k are as defined in claim 1.

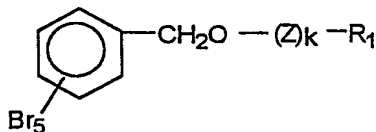
9. A fire retarded composition according to claim 8, wherein said polymer is selected from the group consisting of chlorinated polyethylene, polyethylene, polypropylene, styrene resins, high-impact polystyrene, polyvinyl chloride, acrylonitrile-butadiene-styrene copolymer, flexible and rigid polyurethane, epoxy resins and unsaturated polyester resins.
10. A fire retarded composition according to claim 9, wherein said polymer is polypropylene.
11. A fire retarded composition according to claim 9, wherein said polymer is high impact polystyrene (HIPS).
12. A fire retarded composition according to claim 9, wherein said polymer is acryl-butadiene-styrene terpolymer (ABS).
13. A fire retarded composition according to claim 9, wherein said polymer is polyurethane.
14. A fire retarded composition according to claim 8, wherein said polymer is selected from the group consisting of polyurethane, polypropylene copolymer, high impact polystyrene (HIPS) and acryl-

butadiene-styrene terpolymer (ABS), and said pentabromobenzyl alkyl ether is selected from the group consisting of:

- (i) pentabromobenzyl-O-CH₂-CH₂OCH₃;
- (ii) pentabromobenzyl-O-CH₂CH₂O(CH₂)₃CH₃;
- (iii) pentabromobenzyl-O-(CH₂CH₂O)₂CH₃;
- (iv) pentabromobenzyl-O-(CH₂CH₂O)₂H;
- (v) pentabromobenzyl-O-(CH₂)₆OH;
- (vi) pentabromobenzyl-O-CH₂CH(C₂H₅)(CH₂)₃CH₃; and
- (vii) pentabromobenzyl-O-CH₂CH₂OCH₂CH=CH₂.

15. A fire retarded composition according to any one of claims 8 to 14, further comprising a metal oxide, preferably Sb₂O₃.

16. A process for the preparation of a pentabromobenzyl alkyl ether of the formula:



wherein Z, R₁ and k are as defined in claim 1, comprising reacting a glycol, a mono-, or di-alcohol of the formula HO-(Z)_k-R₁, wherein Z, R₁ and k are as defined in claim 1, or the corresponding metal alcoholate thereof, with a pentabromobenzyl halide, preferably pentabromobenzyl bromide, optionally in the presence of a base.

17. A pentabromobenzyl alkyl ether according to claim 1, for use as a fire retardant, substantially as described and exemplified in the specification.

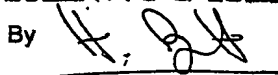
18. A process for the preparation of pentabromobenzyl alkyl ethers as defined in claim 1, substantially as described and exemplified in the specification.

19. A fire retarded polymer composition comprising pentabromobenzyl alkyl ether according to claim 1, substantially as described and exemplified in the specification.

לוצאטו און לוצאטו

LUZZATTO & LUZZATTO

By



ע"י

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.